

Relativistic Density Functional Approach to Open Shells

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ABSTRACT: A full application of relativistic spin-density functional theory in noncollinear treatment of the exchange and correlation field is given to open-shell atoms and ions of the carbon group. It is shown that the influence of noncollinearity is small as compared with self-interaction corrections. Unfortunately, the defect of the local spin-density approximation not to yield a source-free exchange and correlation field increases in noncollinear treatment.
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Introduction

Less than one decade after the formulation of the theorems by Hohenberg and Kohn,¹ the first relativistic generalization was published.² Later, several systematic attempts were made to base four-current density functional theory (CDFT) on quantum electrodynamics (see refs. 3–5 and the recent review ref. 6). For a long time, density functional theory (DFT) suffered from representability problems, and the final approach by Lieb⁷ to solve these problems was rather independent of the first theorem by Hohenberg and Kohn, which states the one-to-one correspondence between ground-state densities and external potentials. The

remaining representability problem of Lieb's approach can be eliminated by confining the systems under consideration in a box of finite volume.⁸ Lieb's approach traces the existence of the universal density functional back to simple convexity properties of the ground-state energy as a functional of the external field and, hence, uncovers the logical roots of DFT. This approach readily carries over to CDFT. The corresponding derivation is explicitly given for the first time in what follows.

In the standard Kohn–Sham approach, the relativistic effects are separated into those entering the kinetic energy functional of the noninteracting reference system (kinematic effects including mass term and spin-orbit coupling) and those entering the exchange and correlation (XC) energy functional. It is expected that the most important effect of the latter type is that of orbital magnetism; however, there does not yet exist a solution to that

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problem, which resides in the orbital current dependence of the XC functional. The (nonrelativistic) current density functional⁹ does not lead to essential improvements of the orbital magnetic moment of $3d$ magnets.¹⁰ If one neglects dependencies on orbital current, there are still relativistic corrections to a nonpolarized homogeneous electron liquid.⁴ It turns out that for atoms and molecules existing in nature, and for moderate strength of a possible external magnetic field, the latter are much smaller than the former two,¹¹ and with the present-day level of accuracy of theoretical description the latter may be neglected.

Even the spin density approximation to XC, which completely neglects XC effects of orbital currents, has almost never been fully employed in the literature. (See ref. 12 for a rare exception.) Usually, it is used with a collinear approximation of the spin polarization inside atomic volumes.

In this study, we present a thorough analysis of the limits of relativistic spin density functional theory as it is available nowadays. To begin, we define, in the next section, the ground state of an inhomogeneous quantum-electrodynamical system. In the third section, we derive the Kohn-Sham-Dirac equations within Lieb's approach of Legendre transforms. Then, in the fourth section, we discuss the various approximations to the density functionals in use, and, finally, results for open-shell atoms and ions are presented and conclusions are drawn.

Quantum-Electrodynamical Ground-State Energy

The basic concern of density functional theory is the ground-state energy of an *inhomogeneous*, interacting, many-particle system as a function of the external potential acting on its density (and possibly as a function of the particle number, allowing for the consideration of ionization energies, affinities, and excitation gaps). In a systematic relativistic treatment of the adiabatic approach to an atom, an ion, or to a molecule with fixed positions of the nuclei (and fixed orientation of their spin and multipolar moments of charge), the electron subsystem would have to be considered as a quantum-electrodynamical system in a static external classical field, $F^{\mu\nu}$, produced by the nuclei and possibly, in addition, by some laboratory device and described by the four-potential:

$$A^\mu(x^\sigma): \partial_0 F^{\mu\nu} = \partial_0(\partial^\nu A^\mu - \partial^\mu A^\nu) = 0 \quad (1)$$

We use the four-coordinate and Minkowski's metric, according to:

$$(x^\sigma) = (ct, x, y, z), \quad g^{\mu\nu} = \text{diag}(1, -1, -1, -1) \quad (2)$$

Of course, the static condition refers to a certain distinguished reference frame.

The Hamiltonian in question is:

$$\hat{H}_A = \int d^3r \left(\hat{\mathcal{H}} - e \hat{j}^\mu A_\mu \right) \quad (3)$$

where the subscript A indicates the (affine-linear) dependence on the external four-potential A , the operator:

$$\hat{j}^\mu = c : \hat{\bar{\psi}} \gamma^\mu \hat{\psi} : \quad (4)$$

is the four-current density operator of the electron-positron field, and:

$$\begin{aligned} \hat{\mathcal{H}} = & : \hat{\bar{\psi}} (-i \boldsymbol{\gamma} \cdot \nabla + mc) \hat{\psi} : - e \hat{j}^\mu \hat{A}_\mu \\ & + \frac{1}{2} : (\epsilon_0 \hat{\mathbf{E}}^2 + \mu_0 \hat{\mathbf{H}}^2) : \end{aligned} \quad (5)$$

(The colons for normal order of \hat{j}^μ were already included in the definition of the four-current density operator and need not be repeated in the second term of $\hat{\mathcal{H}}$; because $\hat{\psi}$ and \hat{A}^μ commute, no reordering of the product is needed.) The field operator, \hat{A}^μ , describes the field created in the quantum-electrodynamical system and is to be distinguished from the external (c -number) field A^μ in eqs. (1) and (3). Furthermore:

$$\hat{\mathbf{E}} = -c(\partial_0 \hat{\mathbf{A}} + \nabla \hat{A}_0), \quad \mu_0 \hat{\mathbf{H}} = \nabla \times \hat{\mathbf{A}} \quad (6)$$

for the internal photonic electric and magnetic fields.

In ref. 8 (section 9.1) it was shown that the ground-state energy was obtained by:

$$\begin{aligned} E[A, Q] = \min_{\Psi, J} \left\{ \langle \Psi | \hat{H}_{A, J}^{\text{eff}} | \Psi \rangle \left| \langle \Psi | \hat{j}^\mu | \Psi \rangle = 0, \right. \right. \\ \left. \left. - \frac{e}{c} \int d^3r J^0(\mathbf{r}) = Q \right\} \end{aligned} \quad (7)$$

where the internal fields, \hat{A}^μ and \hat{j}^μ , are split into mean values, a^μ and J^μ , and fluctuating fields, \hat{a}^μ and \hat{j}^μ , according to:

$$\hat{A}^\mu = \hat{a}^\mu + a^\mu, \quad \langle \Psi | \hat{a}^\mu | \Psi \rangle = \langle \hat{a}^\mu \rangle = 0 \quad (8)$$

$$\hat{j}^\mu = \hat{j}^\mu + J^\mu, \quad \langle \Psi | \hat{j}^\mu | \Psi \rangle = \langle \hat{j}^\mu \rangle = 0 \quad (9)$$

and the effective Hamiltonian of the inhomogeneous quantum field system is:

$$\hat{H}_{A,J}^{\text{eff}} = \int d^3r (\hat{\mathcal{H}}_J^{\text{eff}} - eJ^\mu A_\mu), \quad (10)$$

$$-\frac{e}{c} \int d^3r J^0(\mathbf{r}) = Q$$

$$\hat{\mathcal{H}}_J^{\text{eff}} =: \hat{\bar{\psi}}(-i\boldsymbol{\gamma} \cdot \nabla + mc)\hat{\psi} + \frac{1}{2}:(\epsilon_0 \hat{\mathbf{e}}^2 + \mu_0 \hat{\mathbf{h}}^2):$$

$$- e\hat{J}^\mu \hat{a}_\mu - \frac{1}{2}eJ^\mu a_\mu \quad (11)$$

In the operator part of the Hamiltonian, $\hat{H}_{A,J}^{\text{eff}}$, correlation and all vacuum polarization processes are retained. The corresponding states may be restricted to those obeying $\partial_\mu \hat{a}^\mu |\Psi\rangle = 0$ and containing transversal photons of the field \hat{a}^μ only. Note that, for reasons that become clear in what follows, we have not transformed the first term of eq. (11): $\hat{\psi}$ is still connected with the full four-current according to eq. (4).

The content of this section may appear rather esoteric to readers who are aware of unsolved problems with quantum fields; however, we use it as a guide to build up and assess the various models of density functional theory considered.

Current-Density Functionals and Kohn–Sham–Dirac Equation

Because $E[A, Q]$ is convex in Q , we introduce the Legendre transform (cf. ref. 8, chapter 5):

$$-\tilde{G}[A, w] \stackrel{\text{def}}{=} \sup_Q \{wQ - E[A, Q]\}, \quad (12)$$

$$E[A, Q] = \sup_w \{Qw + \tilde{G}[A, w]\}$$

Clearly, $E[A, Q]$, as defined by eq. (7), has the gauge property:

$$E[A^\mu + \delta_0^\mu w/c, Q] = E[A, Q] + Qw \quad (13)$$

with a potential constant, w , and hence:

$$\tilde{G}[A, w] = \tilde{G}[A^\mu - \delta_0^\mu w/c, 0]$$

$$\stackrel{\text{def}}{=} G[A^\mu - \delta_0^\mu w/c] \quad (14)$$

$$G[A] = \inf_Q E[A, Q], \quad (15)$$

$$E[A, Q] = \sup_w \{Qw + G[A^\mu - \delta_0^\mu w/c]\}$$

The potential constant, w , plays the role of an electrochemical potential.

Together with $E[A, Q]$, $G[A]$ is concave in A . This suggests the functional Legendre transform:

$$H[J] \stackrel{\text{def}}{=} \sup_A \{G[A] - \text{tr}(JA)\}, \quad (16)$$

$$G[A] = \inf_J \{\text{tr}(AJ) + H[J]\}$$

where we introduced a trace notation:

$$\text{tr}(AJ) \stackrel{\text{def}}{=} -e \int d^3r A^\mu(\mathbf{r}) J_\mu(\mathbf{r}) \quad (17)$$

If we combine eq. (16) with eq. (15), we have the final definition of the four-current density functional:

$$H[J] = \sup_A \inf_Q \{E[A, Q] - \text{tr}(JA)\} \quad (18)$$

from which the ground-state energy may be obtained by:

$$E[A, Q] = \sup_w \inf_J \{Qw + \text{tr}((A^\mu - \delta_0^\mu w/c)J) + H[J]\}$$

$$= \inf_J \sup_w \{Qw + \text{tr}((A^\mu - \delta_0^\mu w/c)J) + H[J]\}$$

$$= \inf_J \left\{ \sup_w [Qw - \text{tr}((\delta_0^\mu w/c)J)] + \text{tr}(AJ) + H[J] \right\} \quad (19)$$

The validity of the saddle-point condition $\sup \inf = \inf \sup$ is, of course, a special issue. For the corresponding nonrelativistic case see ref. 8.

Because the last supremum is $+\infty$ unless $Q = -(e/c) \int d^3r J^0(\mathbf{r})$, the final variational principle for the ground-state energy is:

$$E[A, Q] = \inf_J \left\{ \text{tr}(AJ) + H[J] - \frac{e}{c} \int d^3r J^0(\mathbf{r}) = Q \right\} \quad (20)$$

Besides the convexity properties of $E[A, Q]$ and the gauge property, (13), no physics was used in deriving eqs. (18) and (20). Some further physics enters in when the mutual, dual-functional spaces of admissible four-current densities J and four-potential A are defined. Without going into detail, but guided by nonrelativistic physics (ref. 8, section 6.1), we demand the components of J to be cubic summable functions in the finite volume, V ,

of the large box enclosing the system, and the components of A to be $3/2$ -summable functions. Then, the infima in eqs. (18) and (19) are minima, and the Euler–Lagrange equation can be applied to eq. (20). This is how far a more or less rigorous theory can be pushed at present, independent of the state of art of quantum field theory. At least all representability problems of earlier versions are removed here.

To bring in essential physics into eq. (20), model guesses have to be made for $H[J]$. The standard approach is to split off from $H[J]$ a part corresponding to a closely related solvable reference system and to treat the rest as a local density approximation (LDA) in the spirit of Thomas and Fermi.

A solvable case is a relativistic interaction-free electron–positron system in an external field, which is obtained by replacing $\hat{\mathcal{H}}$ of eq. (5) with:

$$\hat{\mathcal{H}}^0 = : \hat{\psi}(-i\boldsymbol{\gamma} \cdot \nabla + m_0 c) \hat{\psi} : \quad (21)$$

(The difference of masses, $m - m_0$, amounts to mass renormalization caused by interaction, which reduces in the nonrelativistic case to the exclusion of self-interaction.) We denote the pendant of the functional $H[J]$ by $K[J]$ and relate both functionals to each other by writing:

$$H[J] = K[J] - \frac{e}{2} \int d^3r J^\mu a_\mu + E_{\text{xc}}[J] \quad (22)$$

which defines $E_{\text{xc}}[J]$. This leads to the most general Kohn–Sham–Dirac equation^{5,8,13}:

$$\begin{aligned} & \left[ic\boldsymbol{\alpha} \cdot \nabla + \beta m_0 c^2 - ec\boldsymbol{\gamma}^\mu (A_\mu + a_\mu + a_\mu^{\text{xc}}) \right] \psi_k \\ & = \psi_k \varepsilon_k \end{aligned} \quad (23)$$

with the Kohn–Sham exchange and correlation four-potential:

$$-ea_\mu^{\text{xc}} \stackrel{\text{def}}{=} \frac{\delta E_{\text{xc}}[J]}{\delta J^\mu} \quad (24)$$

and the four-current density:

$$J^\mu = c \sum_{k=1}^N \bar{\psi}_k \gamma^\mu \psi_k \quad (25)$$

This is exactly the place where the theory could be improved in a systematic manner—that is, by finding a rigorous $K[J]$ for a reference system closer to reality than eq. (21) and such that the remaining functional that would replace $E_{\text{xc}}[J]$ would depend on J in a sufficiently local manner in the Thomas–Fermi sense.

Approximations

Recall that if quantum electrodynamics were to be taken literally, the amount of mass renormalization, $m - m_0$, would be infinite due to an infinite self-interaction of an electron via its own electromagnetic field. This basic field-theoretic defect prevents *ab initio* treatment of mass renormalization. Due to lack of anything better, one substitutes m_0 by the phenomenological electron mass m and simultaneously excludes the static self-interaction contributions from $E_{\text{xc}}[J]$ as in nonrelativistic theory.

In all approaches derived from LDA, even this exclusion of the self-interaction contributions from $E_{\text{xc}}[J]$ cannot be done rigorously, except for situations of spatially completely separated orbitals. This self-interaction-corrected LDA (SIC-LDA) leads to orbital-dependent expressions¹⁴ that have to be combined with the functional $K[J]$ of eq. (22), because this functional is orbital-derived.

Next, diamagnetic effects form the hard and up to present time unsolved problem of the theory as they are intrinsically nonlocal. Therefore, one uses the Gordon decomposition of the three-current:

$$\mathbf{J} = \mathbf{I} + \frac{1}{m} \nabla \times \mathbf{S} + \frac{\partial \mathbf{G}}{\partial t} \quad (26)$$

into the orbital current density:

$$\mathbf{I} = \frac{1}{2m} \sum_{k=1}^N \bar{\psi}_k (-i\overleftarrow{\nabla} + i\nabla + 2e\mathbf{A}) \psi_k \quad (27)$$

and the spin-current density derived from the spin density:

$$\mathbf{S} = \frac{1}{2} \sum_{k=1}^N \bar{\psi}_k \boldsymbol{\Sigma} \psi_k, \quad \Sigma_l = \begin{pmatrix} \sigma_l & 0 \\ 0 & \sigma_l \end{pmatrix} \quad (28)$$

where σ_l are the Pauli matrices. The last term of eq. (26) vanishes in a stationary situation.

The total stationary current density must have zero divergence due to charge conservation. Because the divergence of the spin current density vanishes by its very structure as a curl, the orbital current density must also be divergence-free: $\nabla \cdot \mathbf{I} = 0$. Because \mathbf{I} vanishes at the surface of our box, it may likewise be expressed as a curl of some vector field, \mathbf{L} , to be visualized as an “angular momentum density”:

$$\mathbf{I} = \frac{1}{2m} \nabla \times \mathbf{L} \quad (29)$$

[Recall that an orbital angular momentum *density* cannot properly figure in quantum mechanics, because position and momentum cannot have definite values at the same time. Accordingly, eq. (29) defines \mathbf{L} only up to an arbitrary additive gradient term.]

The total electric current density may then be expressed as:

$$-e\mathbf{J} = \nabla \times \mathbf{M} = -\frac{e}{2m} \nabla \times (\mathbf{L} + 2\mathbf{S}) \quad (30)$$

\mathbf{M} has the dimension of a “magnetization density,” related in a nonrenormalized way to the angular momenta by the Bohr magneton.

This leads to an alternative way of expressing the general Kohn–Sham–Dirac equation:

$$\begin{aligned} & [-i c \boldsymbol{\alpha} \cdot \nabla + \beta m c^2 + V(\mathbf{r}) + v(\mathbf{r}) + v^{\text{XC}}(\mathbf{r})] \psi_k(\mathbf{r}) \\ & - \mu_0 \beta \int d^3 r' (\mathbf{H}(\mathbf{r}') + \mathbf{h}(\mathbf{r}') + \mathbf{h}^{\text{XC}}(\mathbf{r}')) \\ & \cdot \frac{\delta \mathbf{M}(\mathbf{r}')}{\delta \bar{\psi}_k(\mathbf{r})} = \psi_k(\mathbf{r}) \varepsilon_k \end{aligned} \quad (31)$$

(See ref. 8 for a derivation; however, this equation was incorrectly spelled out there.)

By completely neglecting the orbital current \mathbf{I} , that is:

$$\frac{\delta \mathbf{M}(\mathbf{r})}{\delta \bar{\psi}_k(\mathbf{r}')} = -\frac{e}{2m} \boldsymbol{\Sigma} \psi_k \delta(\mathbf{r} - \mathbf{r}') \quad \text{for } \mathbf{I} = 0 \quad (32)$$

one ends up with the simple form of the Kohn–Sham–Dirac equation of spin-density functional theory (SDFT):

$$\begin{aligned} & \left[-i c \boldsymbol{\alpha} \cdot \nabla + \beta m c^2 + V + v + v^{\text{XC}} \right. \\ & \left. + \frac{e \mu_0}{2m} \beta \boldsymbol{\Sigma} \cdot (\mathbf{H} + \mathbf{h} + \mathbf{h}^{\text{XC}}) \right] \psi_k = \psi_k \varepsilon_k \end{aligned} \quad (33)$$

where the magnetic field couples to the spin only. The Kohn–Sham exchange and correlation field \mathbf{h}^{XC} is noncollinear, even in the widely used local-spin-density approximation (LSDA), an important issue that has been taken into account only in recent years. An important defect of the LSDA is, however, that \mathbf{h}^{XC} obtained from this approximation is not source-free as it should be because \mathbf{h}^{XC} is derived from a vector potential.⁸

The potential and field terms in eq. (33) may be combined into a 4×4 potential matrix:

$$W = V + \mu_{\text{Bohr}} \mu_0 \beta \boldsymbol{\Sigma} \cdot \mathbf{H} \quad (34)$$

acting on the bispinor ψ_k (V is further proportional to the unit matrix). If we introduce a 4×4 bispinor density matrix:

$$\nu = \sum_{k=1}^N \psi_k \psi_k^\dagger, \quad n(\mathbf{r}) = \text{tr } \nu(\mathbf{r}), \quad (35)$$

$$\mathbf{M}(\mathbf{r}) = -2\mu_{\text{Bohr}} \mathbf{S}(\mathbf{r}) = -\mu_{\text{Bohr}} \text{tr}(\beta \boldsymbol{\Sigma} \nu(\mathbf{r}))$$

where, together with \mathbf{I} , we neglect \mathbf{L} , then we find:

$$\frac{\delta E_{\text{XC}}}{\delta \nu_{\tau\sigma}} = \frac{\delta E_{\text{XC}}}{\delta n} \frac{\partial n}{\partial \nu_{\tau\sigma}} + \frac{\delta E_{\text{XC}}}{\delta \mathbf{M}} \frac{\partial \mathbf{M}}{\partial \nu_{\tau\sigma}} = w_{\sigma\tau}^{\text{XC}} \quad (36)$$

The exchange and correlation energy functional E_{XC} depends only on n and \mathbf{M} and, according to eq. (35), only the two-diagonal 2×2 blocks of the full bispinor density matrix ν are needed to obtain these numbers. As a consequence, the off-diagonal blocks of w^{XC} according to eq. (36) are zero, in agreement with eq. (34). Moreover, \mathbf{M} is obtained from the difference:

$$\tilde{\nu}_{ss'} = \sum_{k=1}^N (\phi_{ks} \phi_{ks'}^* - \chi_{ks} \chi_{ks'}^*) \quad (37)$$

of the diagonal blocks of ν (ϕ and χ represent the large and small components of ψ). The 2×2 spin density matrix, $\tilde{\nu}$, can be diagonalized by means of an $\text{SU}(2)$ transformation:

$$\tilde{\nu}(\mathbf{r}) = U^\dagger(\mathbf{r}) \text{diag}(\nu_+(\mathbf{r}), \nu_-(\mathbf{r})) U(\mathbf{r}) \quad (38)$$

where the unitary 2×2 matrix, U , in spin space, depends, in the well-known manner, on the direction of \mathbf{M} in \mathbf{r} -space. The LSDA then yields two function expressions:

$$w_{\pm}^{\text{XC}}(\mathbf{r}) = w_{\pm}^{\text{XC}}(n(\mathbf{r}), \nu_+(\mathbf{r}) - \nu_-(\mathbf{r})) \quad (39)$$

from which the upper diagonal block of the matrix, eq. (36), is obtained as:

$$w^{\text{XC}}(\mathbf{r}) = U^\dagger(\mathbf{r}) \text{diag}(w_+^{\text{XC}}(\mathbf{r}), w_-^{\text{XC}}(\mathbf{r})) U(\mathbf{r}) \quad (40)$$

The lower diagonal block of eq. (36) is just its negative. It is of interest to note that, unlike the nonrelativistic case, the trace of $\tilde{\nu}$ is no longer the density n . This trace is reduced by the contribution of the small component: the electron system cannot be fully spin polarized if a nonzero small component of the wave function is present.

In the widely used collinear approximation to the LSDA, the spin moment density \mathbf{M} is projected onto a global magnetization direction which is taken to be the z -axis, and w^{XC} from eq. (36) is

now obtained diagonal. Even nearly all noncollinear implementations use a piecewise collinear approximation, which assumes collinearity within atomic cells and noncollinearity from cell to cell. (See ref. 15 for a recent review.) In this approximation, \mathbf{h}^{XC} cannot be source-free independent of the functional form of $E_{\text{XC}}(n, \mathbf{M})$.

Applications to Open-Shell Atoms and Ions

We have applied the relativistic full noncollinear SIC-LSDA [eqs. (33)–(40)] to open-shell atoms and ions of the carbon group of the periodic table. In each iteration step of the self-consistency cycle, the potential was spherically averaged and the radial Dirac equation was solved for that average. The spherical potential was SIC corrected with the orbitals obtained. The SIC result was then added to the full nonspherical potential matrix, W , and suitable orbitals to increase the angular variational freedom were added before the nonspherical problem was solved variationally.

To demonstrate the influence of various approximations, we give, for comparison, results with collinear treatment of \mathbf{h}^{XC} , in addition to spherical approximation of $v + v^{\text{XC}}$, and finally without SIC.

As one can see from Table I, there is a substantial improvement in total energies with SIC, which amounts to 1 Rydberg for C to more than 50 Rydbergs for Pb. Experimental values are available for C and Si only. For C, agreement with the SIC results is roughly within 0.1 Rydberg, and for Si within 1 Rydberg. The energy corrections, both due to nonsphericity and to noncollinearity, are by contrast a few milli-Rydbergs at most. Regarding the influence of nonsphericity, our results for the light atoms are in agreement with ref. 17 (in which the investigators used a slightly different LSDA functional). Of course, in the 2+ ions, there is no asphericity and no spin polarization, as they have a closed s subshell. Interestingly, however, we find a closed $6p_{1/2}$ subshell for the Pb atom, which indicates $j - j$ coupling in this case. This is in agreement with findings of quantum-chemical calculations.¹⁸ We find that noncollinearity always lowers the energy. The effect is largest for the 1+ ions, which are well apart from closed-subshell situations.

The XC field of the Pb^+ ion in collinear and noncollinear treatment is shown in Figures 1 and 2. One can see that the noncollinearity is strong and results in a large transverse component of the field even in regions where the collinear field is small. Note that Figure 1 is not simply the z -pro-

TABLE I. Total Energies of Carbon Group Atoms and Ions.^a

	Sph	Sph-SIC	Ns-SIC	NsNc-SIC	Exp. ^b
C	−74.958	−75.889	−75.888	−75.888	−75.743
Si	−577.618	−581.156	−581.155	−581.155	−580.02
Ge	−4190.996	−4203.065	−4203.063	−4203.063	
Sn	−12342.539	−12366.043	−12366.041	−12366.042	
Pb	−41803.694	−41859.634	−41859.634	−41859.634	
C ⁺	−74.097	−75.002	−75.004	−75.004	−74.915
Si ⁺	−577.013	−580.545	−580.545	−580.545	−579.42
Ge ⁺	−4190.409	−4202.473	−4202.473	−4202.474	
Sn ⁺	−12341.995	−12365.495	−12365.497	−12365.500	
Pb ⁺	−41803.135	−41859.069	−41859.072	−41859.078	
C ⁺²	−72.285	−73.145	−73.145	−73.145	−73.122
Si ⁺²	−575.813	−579.340	−579.340	−579.340	−578.22
Ge ⁺²	−4189.233	−4201.296	−4201.296	−4201.296	
Sn ⁺²	−12340.913	−12364.410	−12364.410	−12364.410	
Pb ⁺²	−41802.019	−41857.949	−41857.949	−41857.949	

^a Calculated with LSDA in spherical potential approximation and collinear approximation to spin polarization (Sph), with SIC (Sph-SIC), nonspherical treatment (Ns-SIC), and full nonspherical, noncollinear SIC-LSDA (NsNc-SIC). Energies in Rydbergs.
^b From ref. 16.

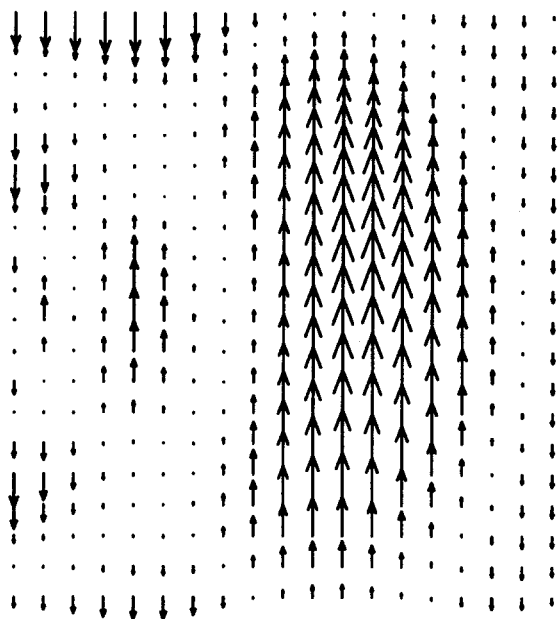


FIGURE 1. XC field of the Pb^+ ion in the nonspherical and collinear approximation. The nucleus is on the left edge at half height and the vertical axis is the direction of the total angular momentum. The edge length of the image is 1-Bohr radius.

jection of the field of Figure 2, because both figures show results of independent, self-consistent calculations. An inhomogeneous collinear XC field cannot, of course, be source-free as demanded by the theory. We find, however, that $\nabla \cdot \mathbf{h}^{\text{XC}}$ is even

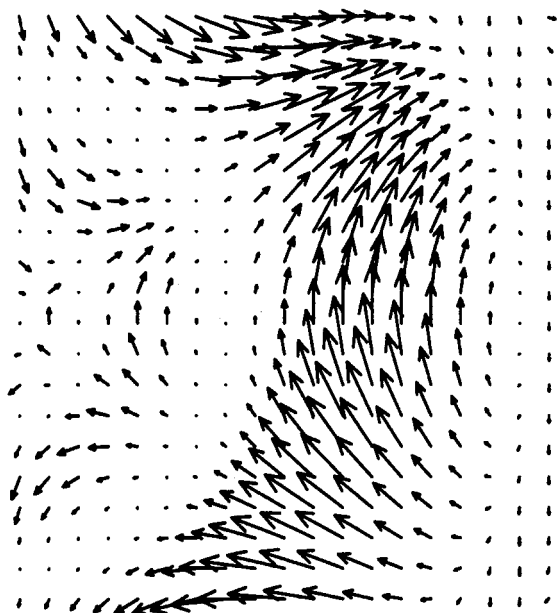


FIGURE 2. The same as Figure 1 in noncollinear treatment.

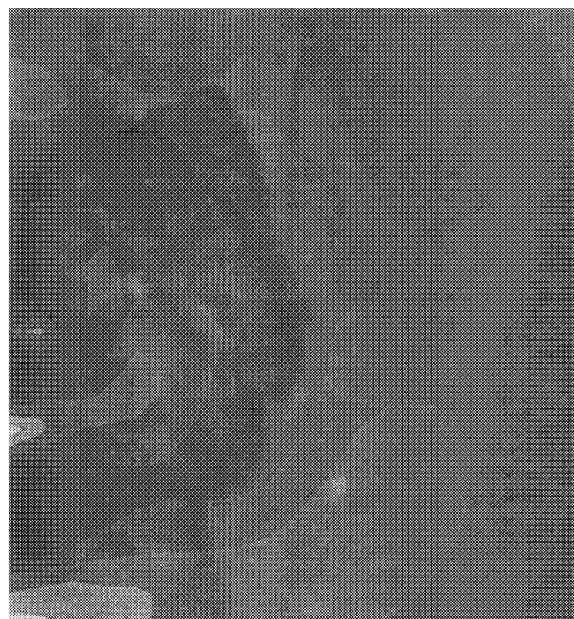


FIGURE 3. The source density of the XC field of Figure 1. The shading is in steps of 0.006 a.u. Light regions have negative values and dark regions have positive values.

appreciably larger in the noncollinear case. The source density of the XC fields of Figures 1 and 2 is shown in Figures 3 and 4, respectively. These results make us unsure whether the intraatomic noncollinear treatment of the LSDA yields im-



FIGURE 4. The source density of the XC field of Figure 2. The shading is the same as in Figure 3.

provement in total energy. Because the difference in total energies obtained from collinear and non-collinear treatment of the LSDA, respectively, is very small, the intraatomic collinear treatment of the LSDA is well justified within the level of accuracy of the LSDA. Improvements including the account of the intraatomic noncollinearity must be investigated outside the framework of the LSDA.

In summary we have shown that relativistic CDFT leads to a source-free XC field that acts on the functional derivative of a full "magnetization density," $\mathbf{M}(\mathbf{r})$, with respect to the Kohn–Sham–Dirac orbital. If orbital current is neglected, this reduces to a potential matrix, $\mu_{\text{Bohr}} \mu_0 \beta \mathbf{\Sigma} \cdot \mathbf{H}$. Within an atom, the latter is usually treated by collinear approximation. We found that the non-collinearity, as well as the nonsphericity, yield only small corrections to the total energy, which are below the present-day accuracy of the density functionals, whereas self-interaction corrections are substantial.

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